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XPS studies of the partial hydrogenation of cyanogen on Pt(111):  
Comparison with HCN and ethylenediamine.

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)  Coadsorption of C <sub>2</sub> N <sub>2</sub> and H <sub>2</sub> on Pt(111) at temperatures above 250 K results in a surface partially hydrogenated surface species. The x-ray photoelectron spectra of this species as well as HCN and ethylenediamine have been obtained, as a function of surface temperature. The partially hydrogenated cyanogen has a N1s binding energy of 399.3 eV, the same as is obtained for partially dehydrogenated ethylenediamine. This is substantially different from the N1s binding energies obtained for HCN adsorbed on Pt(111) which are 397.0 and 398.8 eV. These results strongly favor a di-imine structure for the surface intermediate formed from coadsorption of H <sub>2</sub> and C <sub>2</sub> N <sub>2</sub> on Pt(111).					
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In recent years considerable interest has been shown in the bonding and chemistry of organic cyanides on transition metals [1-15]. In particular, the chemistry of cyanogen and its reaction product with  $H_2$  on the Pt(111) surface has been discussed in detail in a number of previous works from this laboratory [12,14,15]. Results from these studies indicate the presence of a partially hydrogenated cyanogen species (labeled as the gamma state) after coadsorption with  $H_2$ . More specifically, Thermal Desorption Spectroscopy (TDS) and High Resolution Electron Energy Loss Spectroscopy (HREELS) studies have shown that this gamma species forms at -25C and thermally decomposes at 160C leading to desorption of cyanogen and  $H_2$ . A parallel study of the thermal decomposition of ethylenediamine ( $H_2N-CH_2-CH_2-NH_2$ ) on this same surface reveals similar cyanogen and  $H_2$  desorption features also at 160C. HREELS spectra indicate the presence of a surface species with both -NH and -CH bonds and a CN bond order of approximately two. Disappearance of these features near 160C upon sample heating correlates well with TDS results and adds further evidence to the argument in support of a hydrogenated cyanogen species.

However, recent work by Kordesch, et. al. [16,17] on room temperature coadsorption of cyanogen and  $H_2$  on Pd(111) and Pd(100) has been interpreted to show that the product of hydrogenation of cyanogen may be HCN. By analogy with their interpretation of their Pd results, Kordesch, et. al. [16,17] suggest that the gamma state on Pt may be due to HCN formation. We consider the identification of HCN as the gamma state species unlikely since TDS experiments following HCN adsorption on Pt(111) do not show the  $H_2 + C_2N_2$  desorption at 160C characteristic of the gamma state [3]. To shed more light on this interesting reaction system we have carried out XPS studies of  $H_2 + C_2N_2$ , HCN and ethylenediamine on Pt(111).

For this study, x-ray photoelectron (XP) spectra were taken of the Pt(111) surface after exposure of: 1)  $H_2$  coadsorbed with cyanogen, 2) ethylenediamine, and 3) HCN. Exposures were made with the clean Pt crystal held at -70C. A series of anneals



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were then performed in which the crystal was heated to a particular temperature, held at that temperature for 20 seconds, then allowed to cool to -70C or below. After cooling, XP spectra of the N1s core level were collected using MgK $\alpha$  radiation. This sequence of anneal, analyze, etc., etc., was continued to higher temperatures until no N1s emission could be observed. The specific anneal temperatures were derived from TDS spectra of this same system by Kingsley, et.al. [12]. Values were chosen to correlate with formation, dissociation or desorption of various cyanogen species as proposed by Kingsley, et.al. and Lloyd, et.al. Of particular interest in this study are changes which take place between 100C and 170C where the only desorption products are H<sub>2</sub> and C<sub>2</sub>N<sub>2</sub> from the decomposition of the gamma state species.

Figure 1 shows a series of XP spectra over the N1s region for the H<sub>2</sub> + C<sub>2</sub>N<sub>2</sub>/Pt(111) system. Figure 1a, collected after a 100C anneal, shows two peaks of equal intensity at approximately 399.0eV and 397.2eV. Figure 1b, taken after an anneal at 170C, indicates a loss in intensity of the high binding energy feature. The difference spectrum of Figure 1, a-b, indicates that intensity lost from heating to 170C is centered near 399.3eV and also that heating causes some gain in intensity near 397.0eV (reflected by the presence of a negative peak in the a-b spectrum). Figure 2 shows a similar series of spectra for ethylenediamine exposed to this surface. Apart from the difference in relative peak heights in Figure 2a compared with Figure 1a, immediately one notices great similarity between the temperature dependence of the H<sub>2</sub> + C<sub>2</sub>N<sub>2</sub> and the ethylenediamine systems. Most importantly, the difference spectrum of Figure 2 is of very similar shape to that of Figure 1 and indeed shows that heating the ethylenediamine species from 100C to 170C yields a loss of intensity at 399.3eV and gain at 397.0eV, correlating well with H<sub>2</sub> + C<sub>2</sub>N<sub>2</sub> spectra in Figure 1. In contrast, the same set of spectra taken after annealing an HCN exposed surface, Figure 3, display significantly different features from those of figures 1 and 2. The two features in spectrum 3a are shifted to lower binding energy and are quite narrow with respect to

Figures 1a and 2a. Annealing to 170C appears to shift intensity from the high binding energy peak to lower binding energy as evident in the broadening of the low binding energy feature in Figure 3b. The difference spectrum of Figure 3 shows a relatively narrow peak at 398.8eV, substantially different from the features at 399.3eV in Figures 1 and 2.

From the similarity of spectra in Figures 1 and 2 and the obvious differences between those of Figures 1 and 3 we can conclude that the product of the  $H_2 + C_2N_2$  reaction on this surface is not HCN but is more likely the species suggested by Lloyd, et. al. ( $HN=CH=CH=NH$ ). As was pointed out by Lloyd, et. al. the HREELS spectra resulting from the gamma state species provide insufficient information to determine whether the species is HCN or a partially hydrogenated cyanogen. Additional information such as the TDS results from HCN adsorption [3] and the present XPS studies must be taken into account to obtain a clear picture of this system. It should be noted that the chemistry on Pt and Pd may be substantially different. In particular the simple molecular desorption feature for  $C_2N_2$  occurs at 100C on Pt(111) whereas it occurs at <27C on Pd(111). Thus while we feel our data shows that HCN is not associated with the  $H_2 + C_2N_2$  reaction on Pt(111) we can not at present rule out this reaction path on Pd.

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## Figure Captions

Figure 1. N1s region spectra of the Pt(111) surface after hydrogen coadsorption with cyanogen and: a) anneal at 100C, b) anneal at 170C, and a-b) difference spectrum.

Figure 2. N1s region spectra of the Pt(111) surface after ethylenediamine ( $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ) exposure and: a) anneal at 100C, b) anneal at 170C, and a-b) difference spectrum.

Figure 3. N1s region spectra of the Pt(111) surface after HCN exposure and: a) anneal at 100C, b) anneal at 170C, and a-b) difference spectrum.

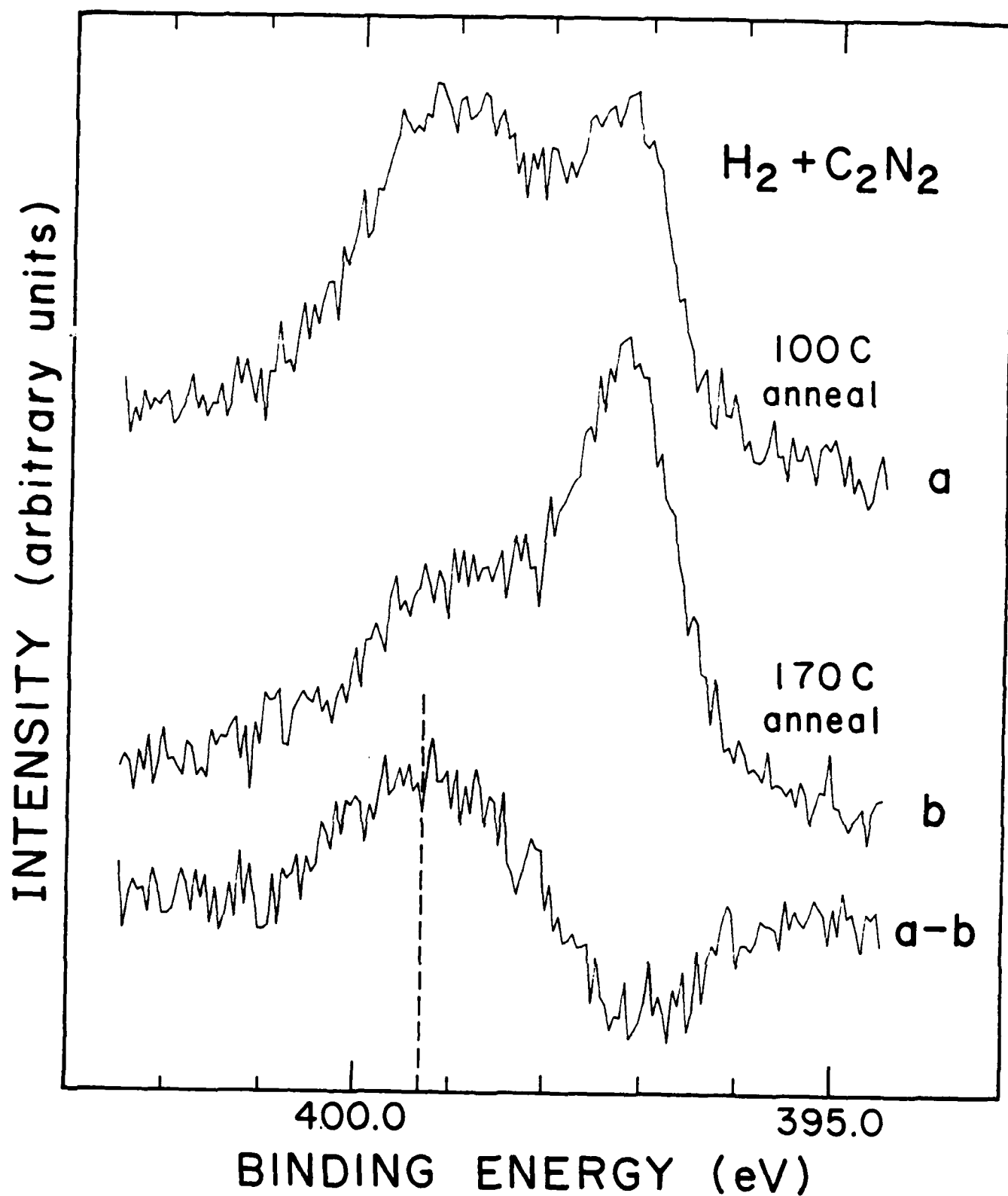


Figure 1.

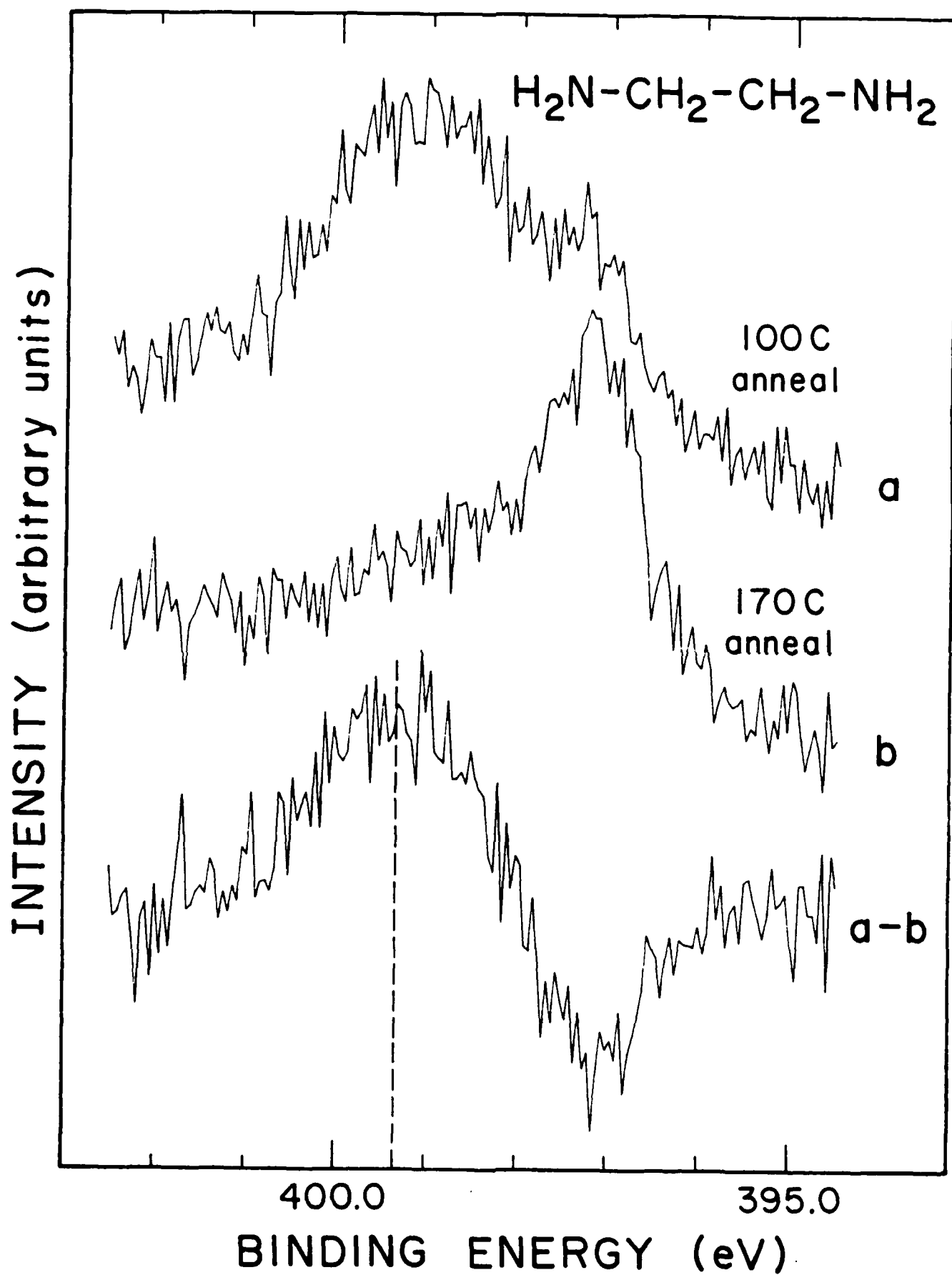


Figure 2.



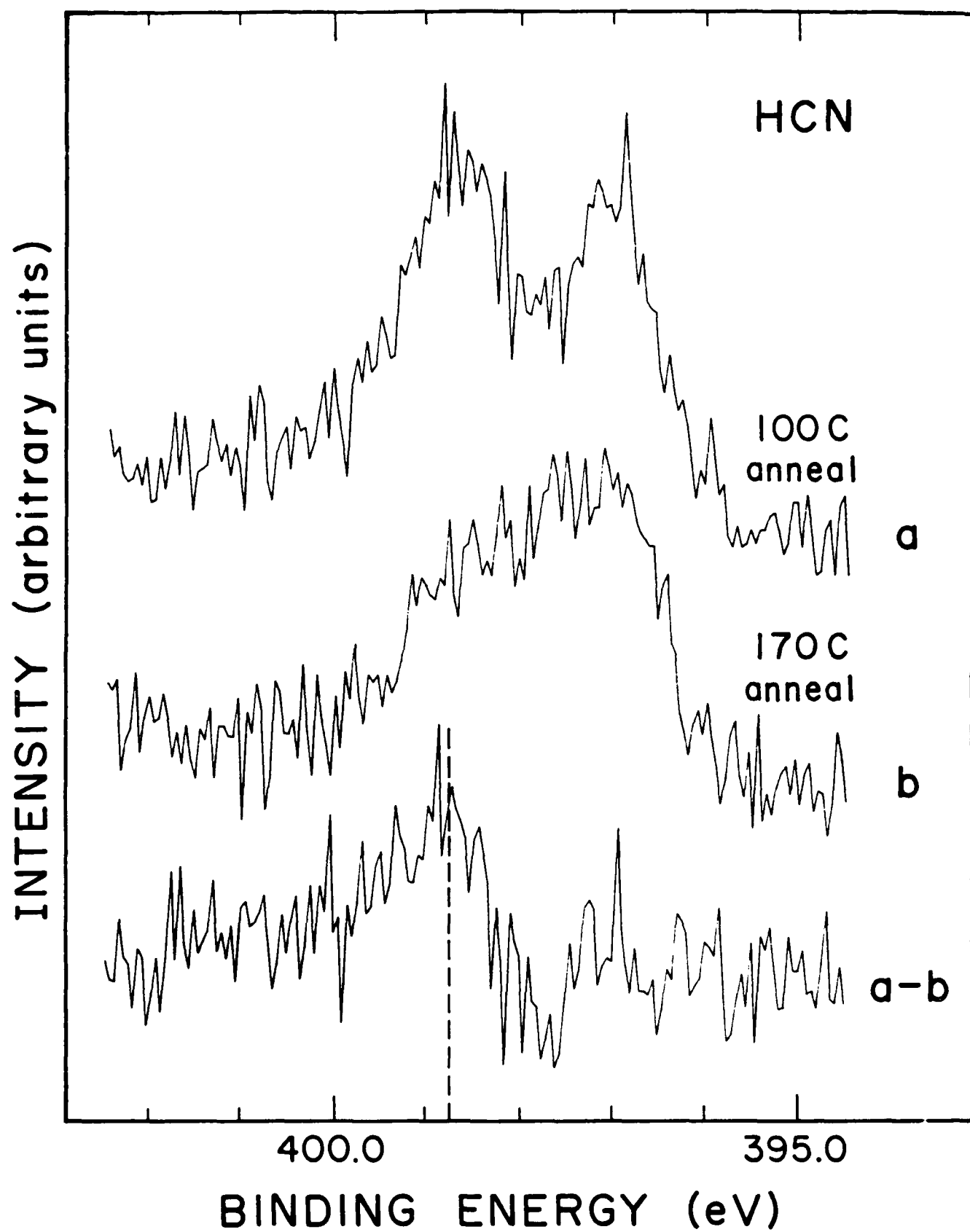


Figure 3.